SiC Powder Production-Quality Control

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Goals of Today’s Presentation

- Provide a better understanding of the relationship the carbothermic production of SiC
- Demonstrate the effects of precursor impurities, reaction time and spatial location on physical and chemical characteristics of SiC for dynamic energy dissipation applications

Global Challenges for SiC

•Need for a blend between metallurgical and ceramic grade SiC

•Varying market need ~800,000 to 1.3M tpa

•Balance between the black and green markets; chemical uniformity in the crystalline market

- particulate diesel filters
- ceramic armor
- semiconductor
- silicon wire cutting saws
- Abrasives
- Varied optics (mirrors)

•Changes from small scale Acheson to large scale, ie Hennepin, IL or Delfzijl, NE

•Cost Challenges

- Energy
- Environment
- Pet coke/coal costs

Wire saw for Si in PV

Particulate diesel filters

IBA Spectra, Kevlar Vest & Helmet
B_4C & SiC Torso & Side Plates

SiC

- SiC is derived in bulk form by pure vapor phase reactions, ie CH_3SiCl_3 – SiC + HCl
- This reaction can be varied by the inclusion of particulate
- Si can be reacted to graphite (particulates or solid preforms) in a solid state reaction; again this can be varied by mixtures of SiC + C
- Solid state sintered or liquid phase sintered SiC

Key in most of these processes is the inclusion of SiC particulate, mostly derived from the carbothermic reduction (Acheson Process) or SiO_2 + C – SiC + CO

Chemical Variations between Carbon Sources

- Acheson processed SiC had many geographically influenced precursor
  - Chinese carbon originates from coal
  - American and European carbon originates from petroleum coke
- Silica can also regionally vary with Fe, Ti and Al typical variants

Petroleum Grade Coke

Properties	Fuel Grade Green	Anode Grade Calcined
Sulfur (wt%)	2.5-5.5	1.7-3.0
Ash (wt %): Si, Fe, Ti	0.1-0.3	0.1-0.3
Nickel (ppm)	<1	165-350
Vanadium (ppm)	200-400	120-350
Residual Hydrocarbon (wt%)	9-12	<0.25

Anthracite Coal

	NIST 1633		NIST 1633a	
Element	NIST value[1] (mean SD)	USGS average[2]	NIST value[1] (mean SD)	USGS average[3]
SI (%)		27±3.3	22.8±0.8	26±2.6
Al		17±2.8	14	18±3.1
Fe		8.0±0.93	9.40±0. 10	11±1.7
Mg		2.2±0.32	.455±0.010	.71±0.14
Ca		5.4±1.2	1.11±0.01	1.3±0.31
Na		.25±0.03	.17±0.01	.16±0.03
K	1.72	1.3±0.15	1.88±0.06	1.5±0.19
Ti		.80±0.15	.8	.85±0.18
Mn	.0493±0.0007	.076±0.11	.0190	.026±0.08
As (µg/g)	61±6	[4]<100	145±15	190±49
B	430	440±46		32±4.0
Ba		1,600±490	1,500	910±160
Be	12	15±1.5	12	14±1.9
Ce		170±29	180	160±53
Co	38	38±4.9	46	38±6.2
Cr	131±2	120±23	196±6	180±33
Cu	128±5	100±25	118±3	93±21
Eu		3.1±0.5	4	3.4±0.6
Ga	49	39±5.8	58	54±11
La		96±13		
Mo			29	28±6.2
Nd		60±15		100±29
Ni	98±3	110±15	127±4	140±19
Pb	70±4	74±9.0	72.4±0.4	76±12
Sc		25±4.0	40	29±5.7
Sr	1,380	1,700±30	830±30	900±140
V	214+8	200+24	300	240+36
Y		53±7.8		
Yb		6.6±0.9		
Zr		180±29		

USGS Bulletin 2144, 1997 Chemistry of Antracite Coal

SiC Production

Country	Capacity (tpa)
USA	50,000
Brazil	43,000
Spain	20,000
Germany	36,000
China	455,000
Switzerland	8,000
France	16,000
Netherlands	65,000
Romania	37,000
South Africa	30,000
Russia	80,000
India	5,000
Japan	60,000
Mexico	30,000
Norway	85,000
Venezuela	40,000
Others	180,000
Total	1,240,000

Sources: IM and USGS, 2007

Large scale furnace capable of 250 tons, i.e. Washington Mills, Hennepin, IL and Kollo Delfzil, NE

Traditional small furnace Acheson process up to 30 tons

This does not include beta-SiC from smaller, fluidized bed producers, ie. Superior Graphite

Acheson processed SiC had many geographically influenced precursor

•Uncertainty of Chinese raw materials
•Reduced production of ceramic grades in North America and Europe

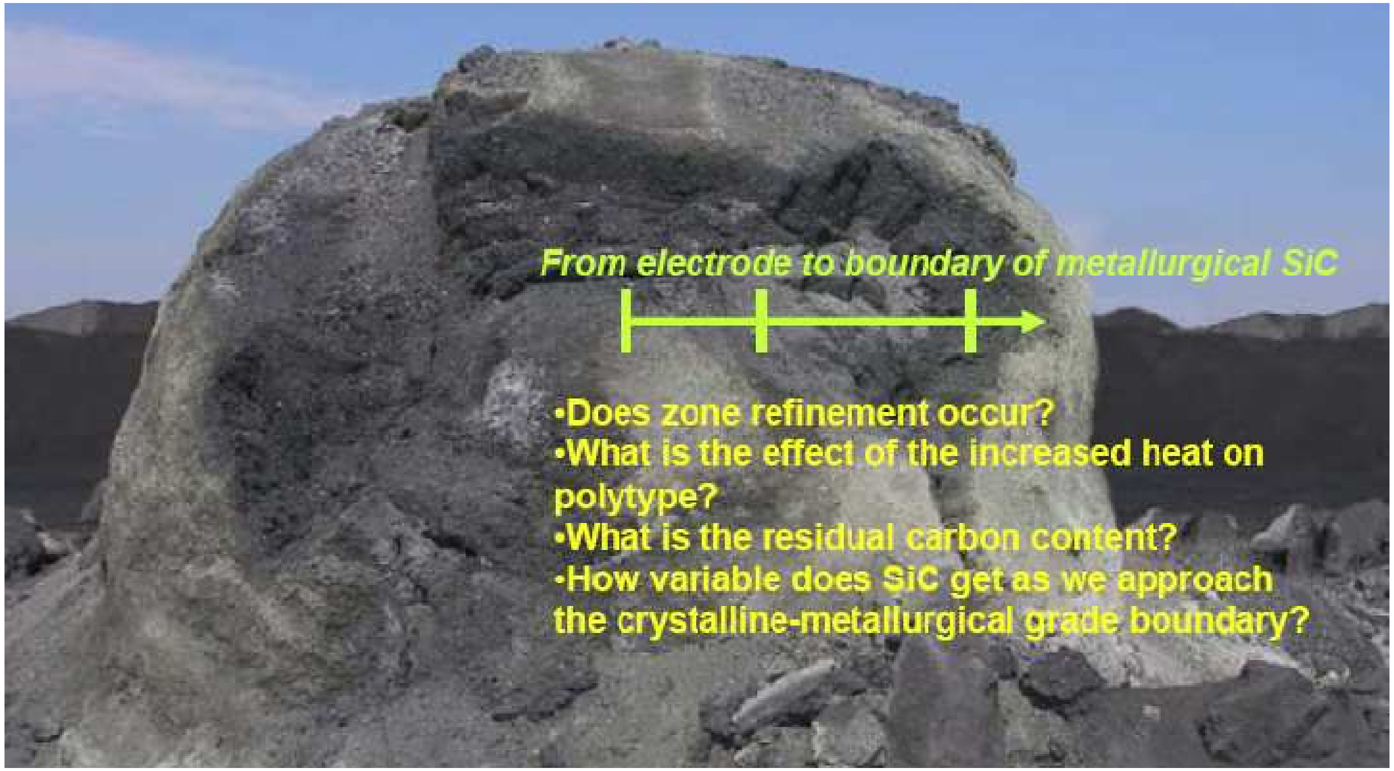
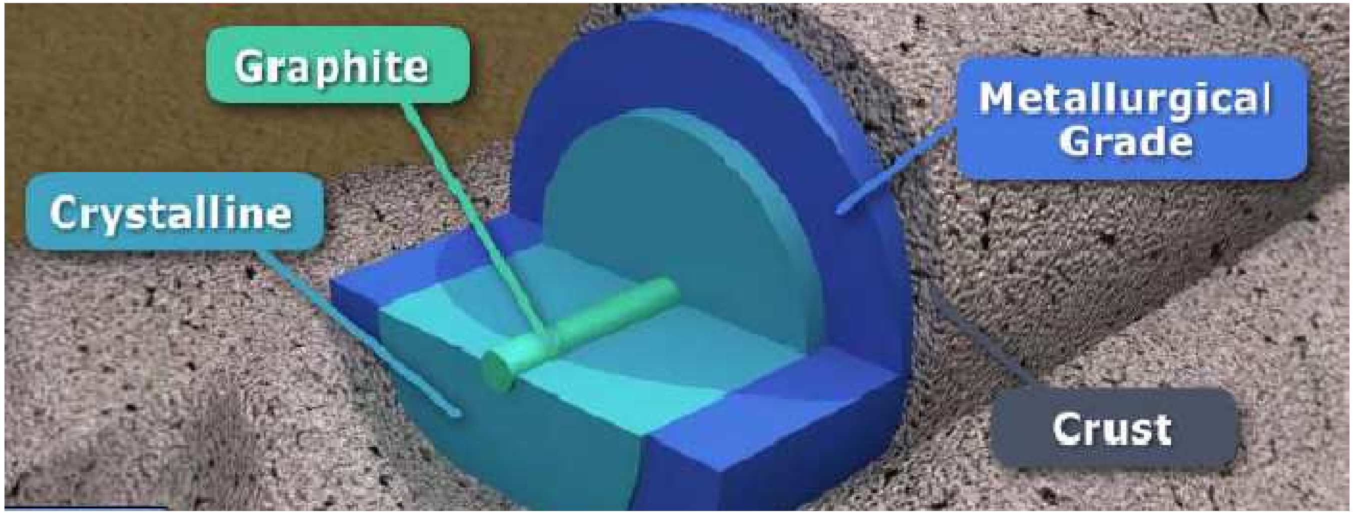


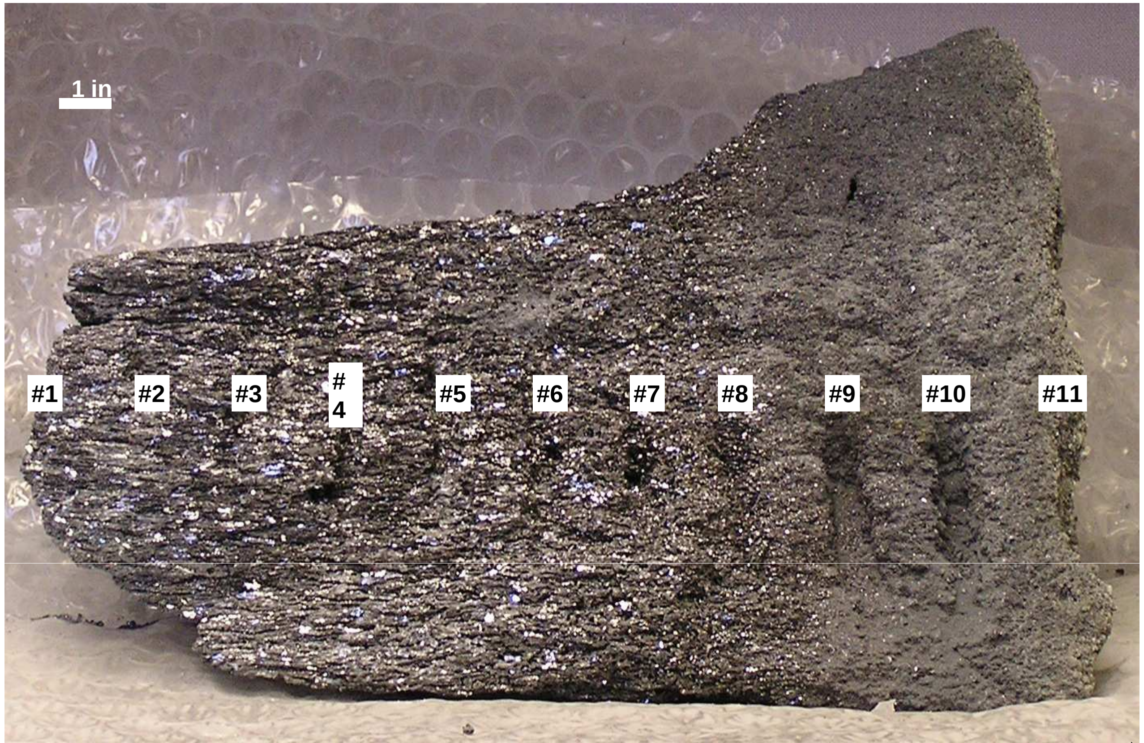
Photo from Washington Mills, Hennepin, IL

SiC Selection/Mining Process



•What is the influence of thermal variation?
•Does zone refinement occur?
•What is the impact of these variations on the chemistry and crystallinity of SiC?

Balance between crystalline and metallurgical SiC



0 2 4 6 8 10 12 14 16 18 20

Distance from electrode edge to metallurgical grade SiC edge (in)

%	1	2	3	4	5	6
SiC	99	99.1	98.8	98.8	98.6	98.2
Free Si	0.06	0.2	0.51	0.55	0.66	0.59
Free C	0.14	0.1	0.07	0.07	0.06	0.09
Al	0.01	0.01	0.01	0.02	0.03	0.07
Fe	0.03	0.03	0.04	0.05	0.07	0.12

Polytypes	1	2	3	4	5	6
6H	Major	Major	Major	Major	Major	Major
33R	4.5	3.4	4.7	4.7	4.7	5.1
4H	1.4	1.1	1.2	1.3	9.5	26
15R	1.1	0.8	0.4	0.4	2.8	1.2
Si	0.4	0.6	1.2	1.6	1.8	0.6

Quality of powder is visually sorted by the producer

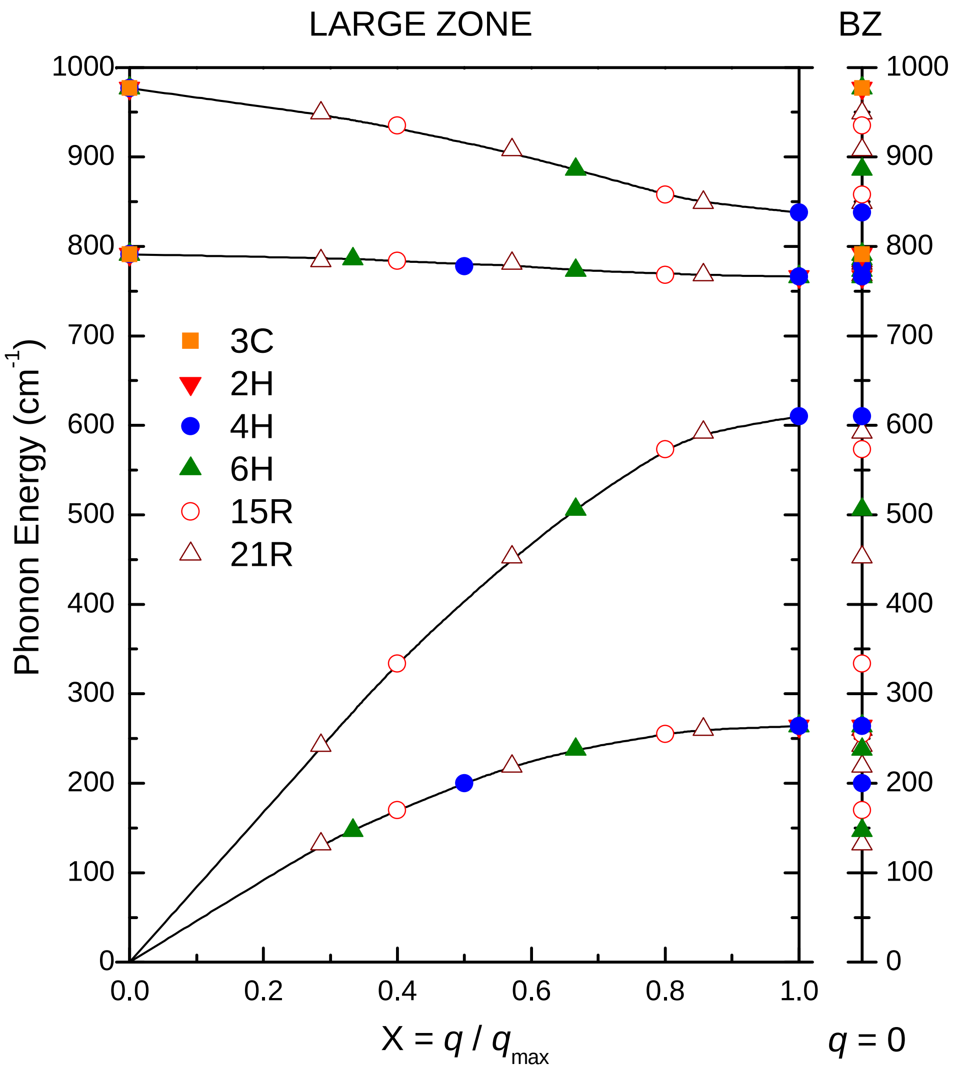
Interpretation of Raman Spectra of SiC Polytypes

• In the large zone (LZ) representation, which unfolds the BZ phonon dispersion curves in the axial direction up to q_{max}, the phonon dispersion curves become nearly independent of polytype.

• Points of this common LZ spectrum accessible to Raman measurements have special values of the reduced momentum $X = q / q_{max}$ that are equivalent to $q = 0$ in the BZ representation. These special points on the phonon dispersion curves in the large zone are characterized by small energy discontinuities for all accessible reduced momentum values, except for X = 0.

• The use of the LZ scheme allows identification of different SiC polytypes by Raman spectroscopy measurement. For example, the band at 510 cm^{-1} is unique in the 6H polytype, whereas the band at 335 cm^{-1} is unique in the 15R polytype.

Ramsdell notation	Atoms per unit cell	Accessible values of X
3C	2	0
2H	4	0, 1
4H	8	0, 1/2, 1
6H	12	0, 1/3, 2/3, 1
15R	10	0, 2/5, 4/5
21R	14	0, 2/7, 4/7, 6/7

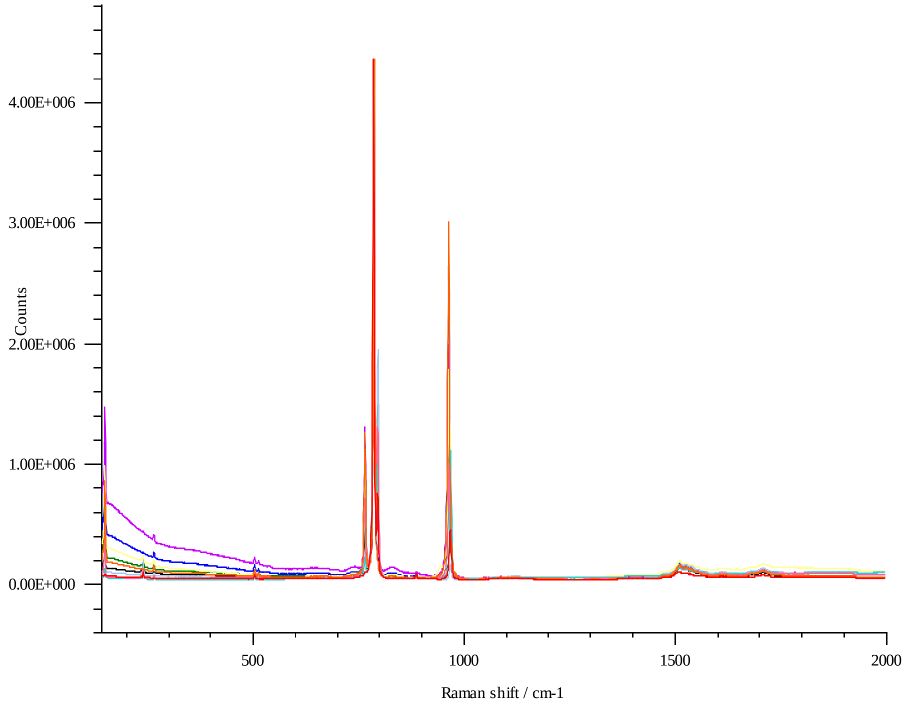


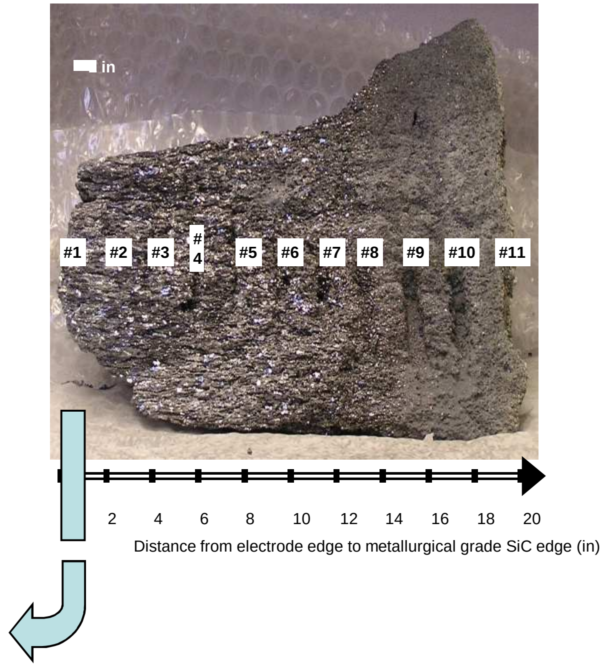
*after L. Patrick *et al*, PR **143** 526, PR **167** 809, PR **170** 698, PR **173** 787

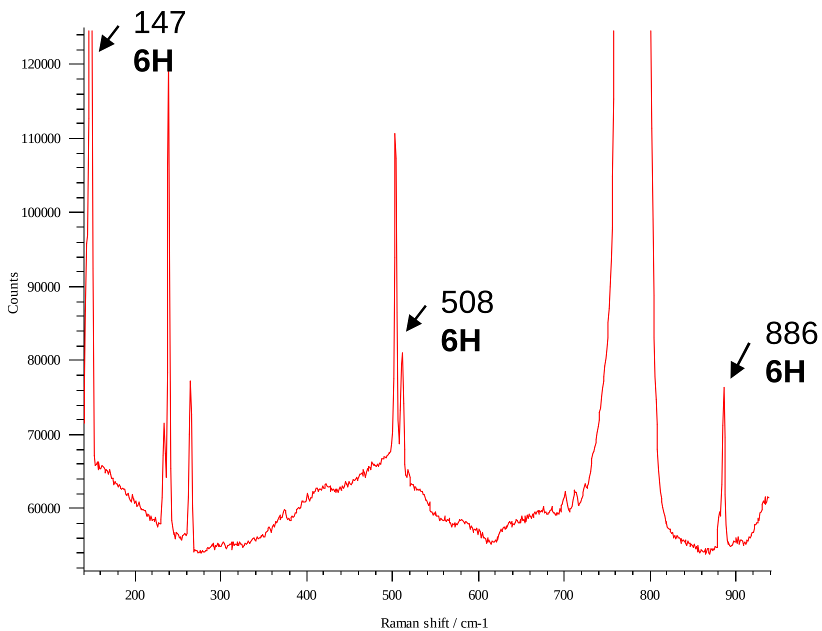
Summary of Raman Analysis

Sample #	Distance from electrode edge, in	SiC polytypes identified (% of all observations)						Graphitic carbon detected	Free silicon detected
		3C	2H	4H	6H	15R	21R		
1	0	+ -	+ -	-	100%	-	-	-	-
2	2	+ -	+ -	-	100%	-	-	-	-
3	4	+ -	+ -	-	100%	-	-	-	-
4	6	+ -	+ -	-	100%	-	-	-	-
5	8	+ -	+ -	10%	80%	-	-	-	-
6	10	+ -	+ -	70%	20%	20%	-	-	10%
7	12	+ -	+ -	40%	30%	10%	-	-	10%
8	14	+ -	+ -	70%	20%	10%	-	10%	-
9	16	+ -	+ -	30%	70%	10%	20%	70%	-
10	18	+ -	+ -	10%	10%	+ -	+ -	70%	-
11	20	+ -	+ -	10%	+ -	+ -	+ -	100%	-

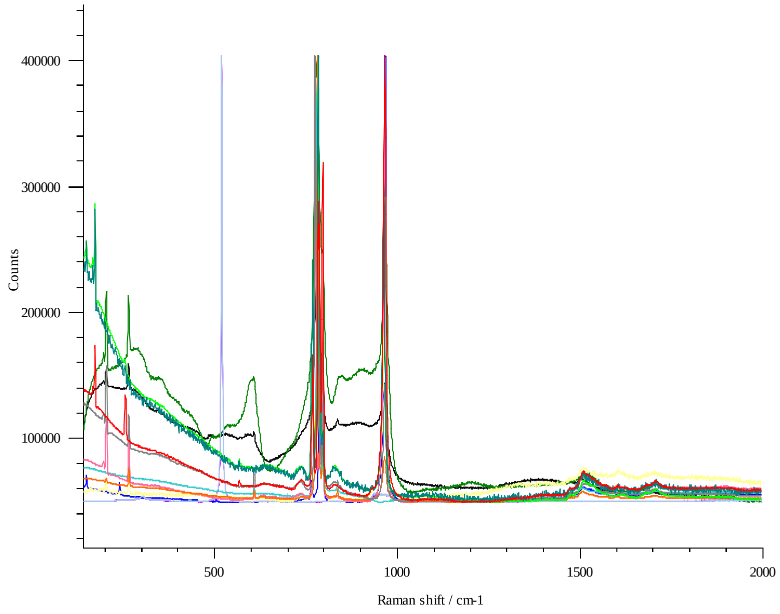
(+ -) unambiguous identification was not possible

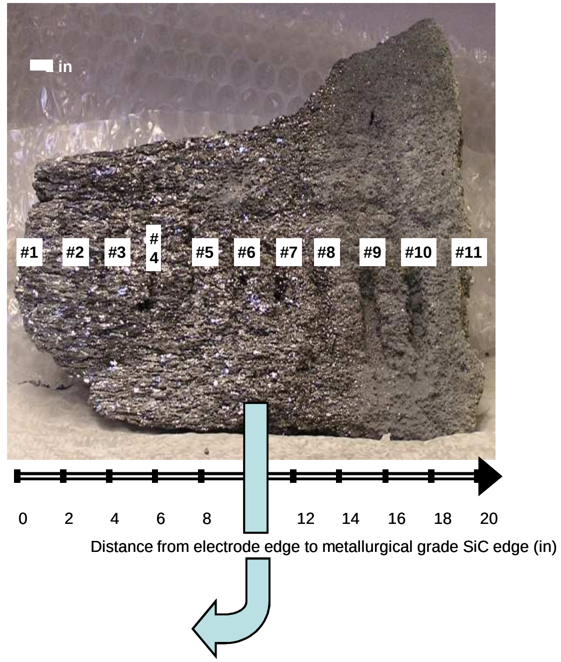

4.00E+006
3.00E+006
2.00E+006
1.00E+006
0.00E+000
Counts
500
1000
1500
2000
Raman shift / cm-1

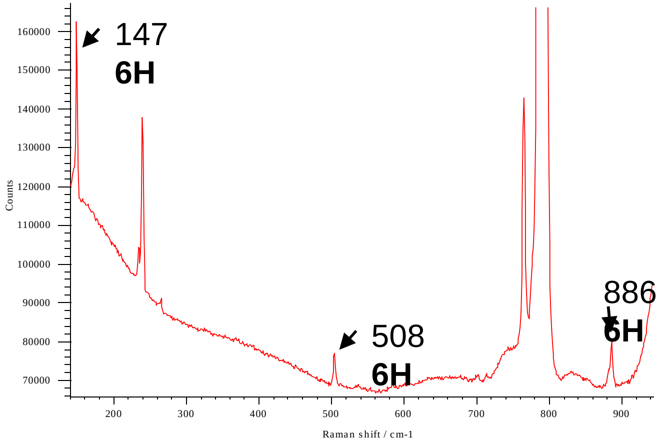

in
#1
#2
#3
#4
#5
#6
#7
#8
#9
#10
#11
2
4
6
8
10
12
14
16
18
20
Distance from electrode edge to metallurgical grade SiC edge (in)

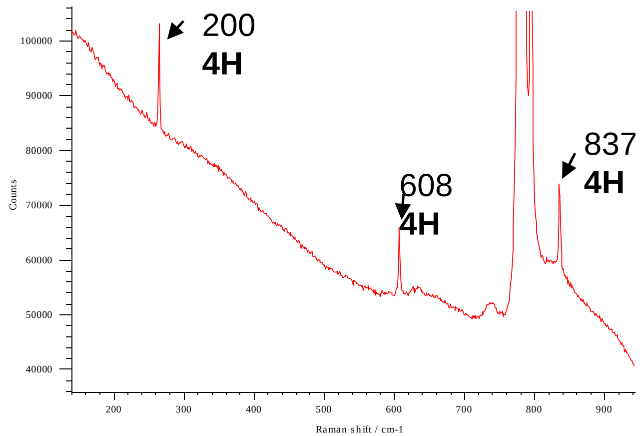

147
6H
508
6H
886
6H
120000
110000
100000
90000
80000
70000
60000
Counts
200
300
400
500
600
700
800
900
Raman shift / cm-1

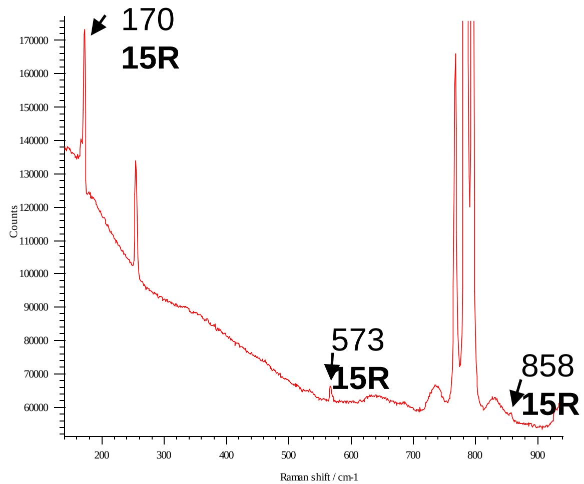
Shift in location adds crystalline variability



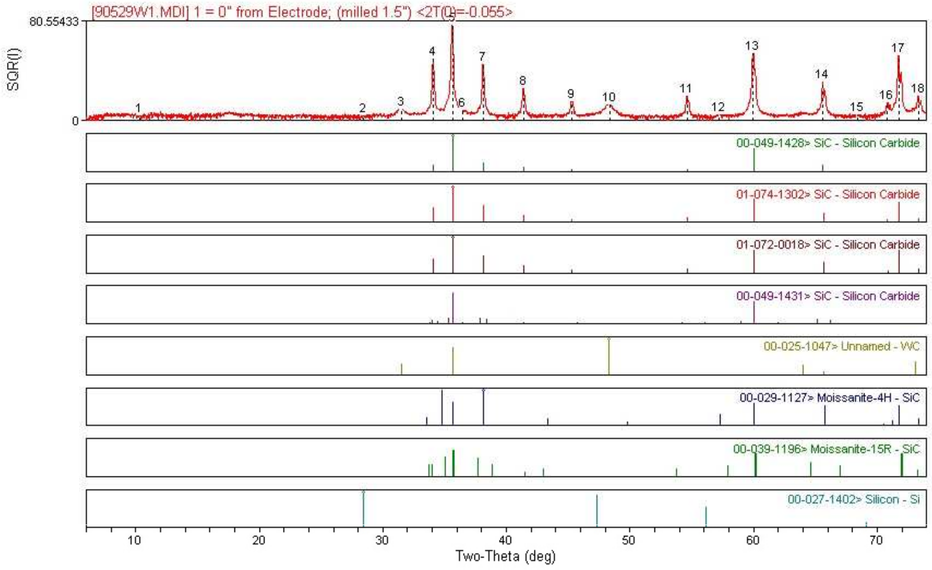


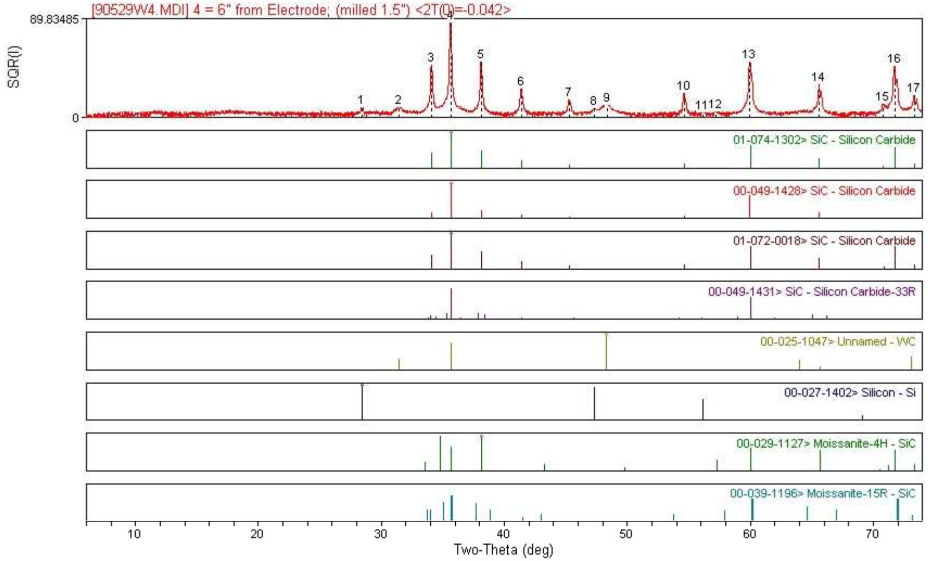




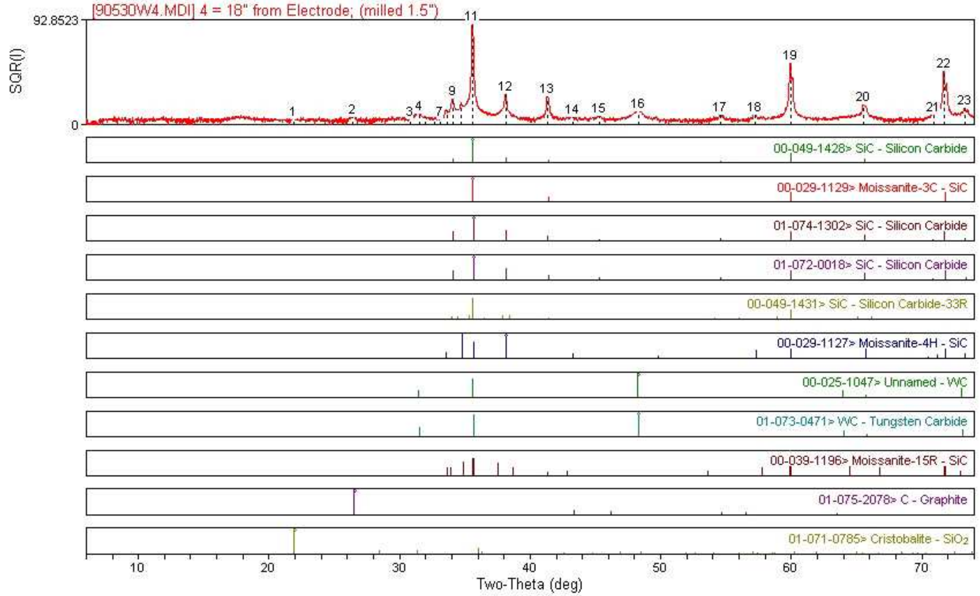


XRD Profiles in an Acheson Furnace





The complexity of the phase mixture increases within the furnace as a function of distance from the hot face



Summary of XRD Analysis

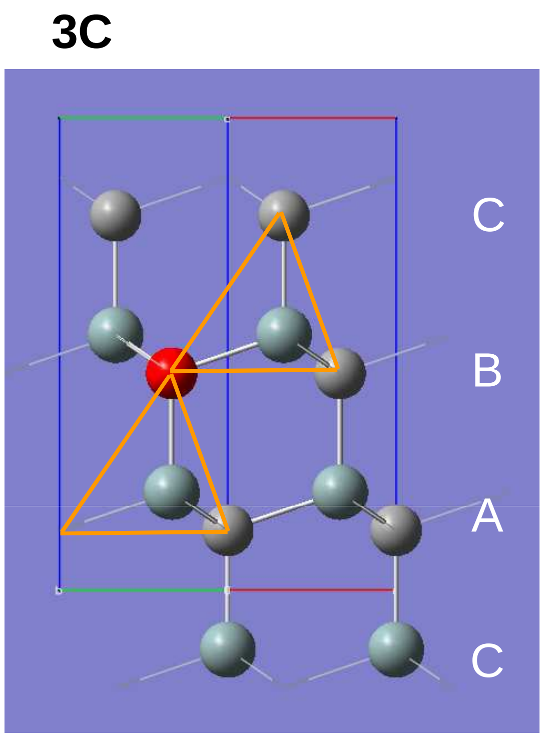
Sample #	Distance from electrode edge, in	SiC polytypes identified (% peak intensity)						Graphitic carbon detected	Free silicon detected
		3C	2H	4H	6H	15R	33R (t)		
1	0	-	-	1.4%	93.0%	1.1%	4.5%	-	0.4%
2	2	-	-	1.1%	94.7%	0.8%	3.4%	-	0.6%
3	4	-	-	1.2%	93.7%	0.4%	4.7%	-	1.2%
4	6	-	-	1.3%	93.6%	0.4%	4.7%	-	1.6%
5	8	+ -	-	9.5%	83.0%	2.8%	4.7%	-	1.8%
6	10	+ -	-	26%	67.7%	1.2%	5.1%	-	0.6%
7	12	+ -	-	63%	26.7%	5.5%	2.5%	0.8%	1.5%
8	14	+ -	-	41%	14.7%	5.5%	4.1%	0.7%	0.6%
9	16	+ -	-	10%	>10%	1.9%	3.6%	12%	-
10	18	+ -	-	4.3%	>10%	0.9%	5.6%	7%	-
11	20	+ -	-	4.6%	>10%	1.0%	5.6%	18%	-

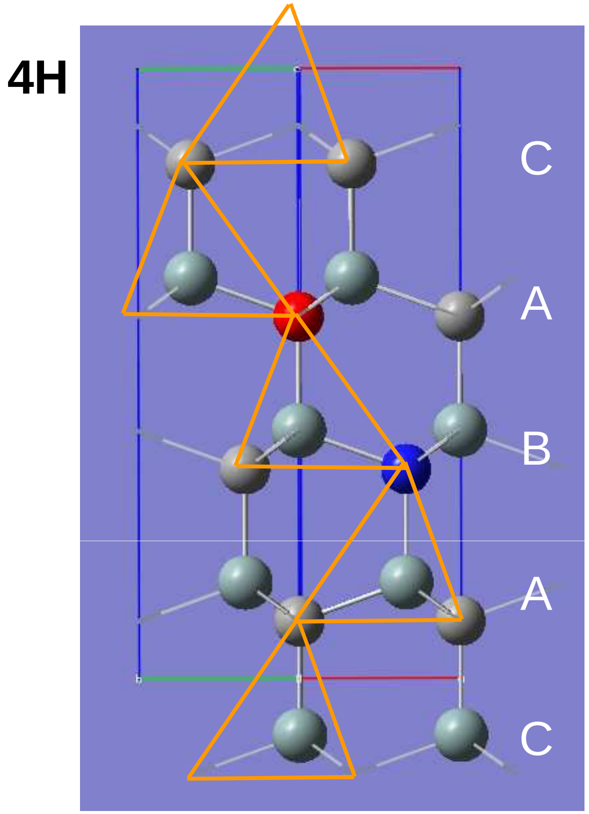
(+ -) unambiguous identification was not possible

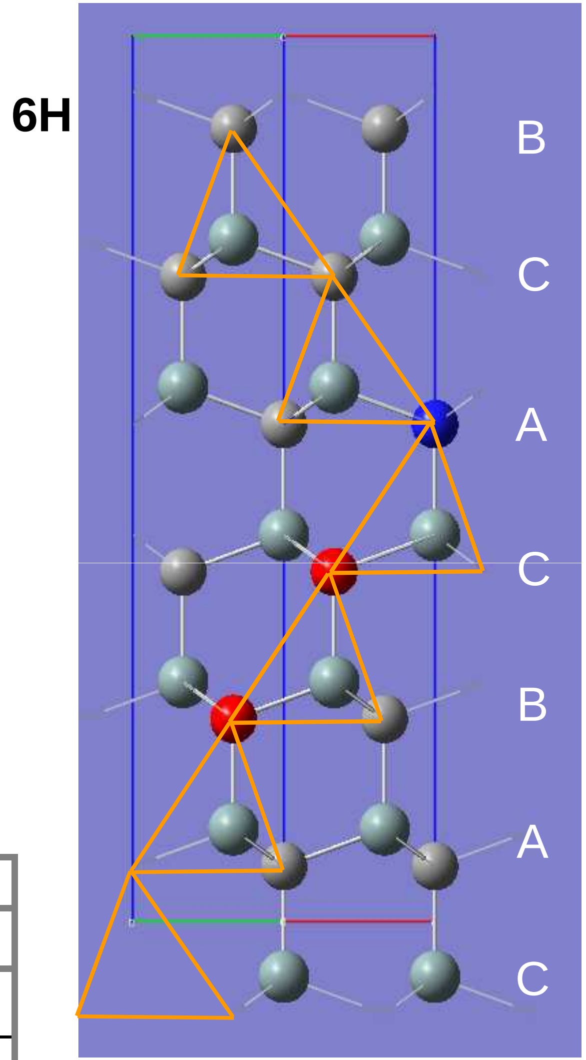
(t) tentative assignment

What is the implication of this variability?

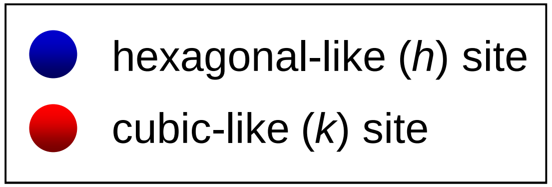
Inequivalent Substitutional Sites in SiC Lattice



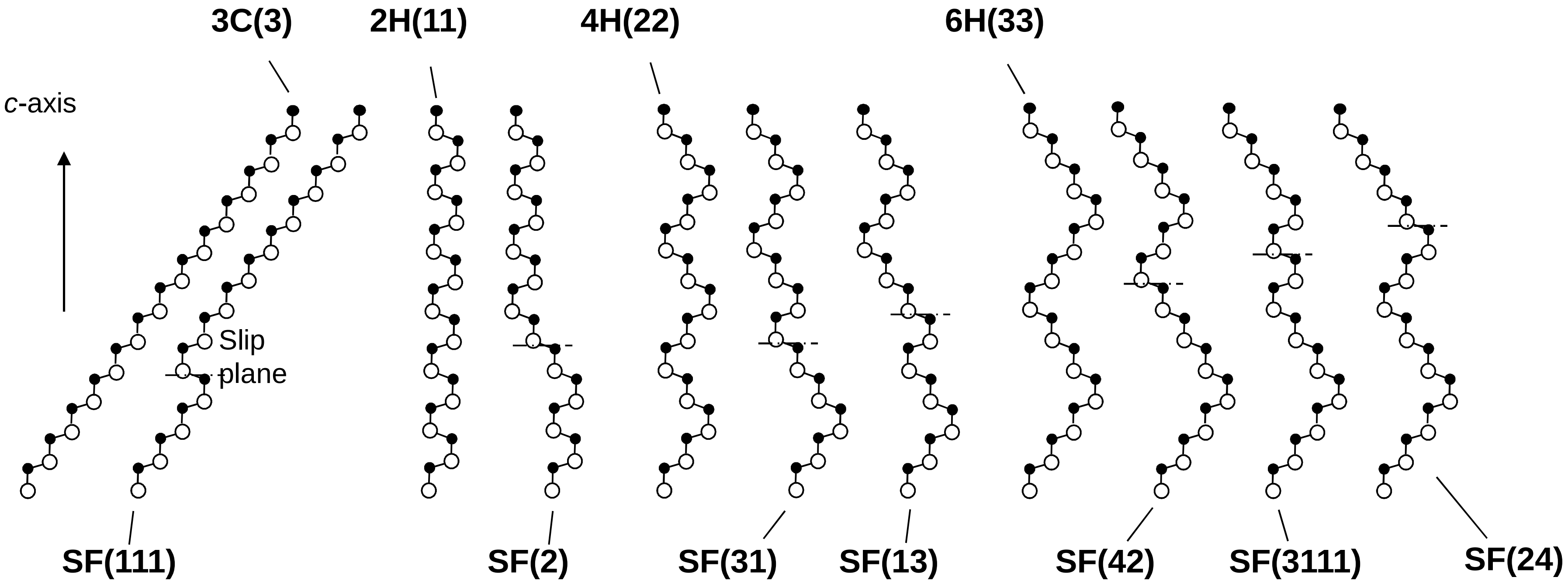




Ramsdell notation	ABC notation	Jagodzinski notation	No. of inequivalent Si (C) sites	
			cubic-like	hexagonal-like
3C (zincblende)	ABC	*k*	1	0
2H (wurzite)	AB	*h*	0	1
4H	ABAC	*hk*	1	1
6H	ABCACB	*hkk*	2	1
15R	ABCACBCABACABCB	*hkkhk*	3	2

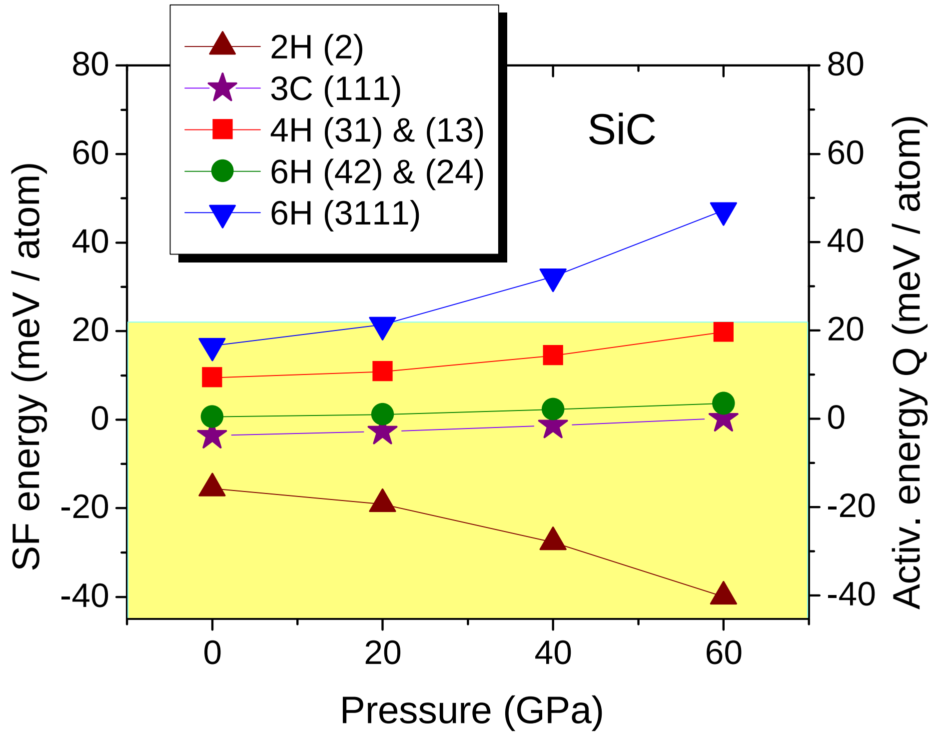


Stacking Faults in SiC Polytypes



Geometrically distinguishable stacking faults (SF) obtained by glide in 3C, 2H, 4H, and 6H SiC in different slip planes (dashed horizontal lines), viewed from a [1120] direction

SFE in SiC as a Function of Pressure Axial Next-Nearest Neighbor Ising (ANNNI) Model for Calculating Stacking Fault Energies



6H (3111) SF is critical for SiC plasticity at elevated pressures

Critical Stress (GPa)	6H (3111)	4H (31) 4H (13)
SiC	20	65

There is real implications to this in processing, ie machining, and in use ie. shock loading during take off

Summary

– SiC powder has beneficial attributes, but many incorrect assumptions have been made regarding it's uniformity
– Powder *"variability"* is characteristic of carbothermic reduced SiC
– High percentage of "non-US" based sources have lead to variable powder
– Properties of SiC polytypes can contribute to the variability of the dense part if not accounted for
– Pressure induced variability of stacking fault activation is an example of how variable polytypes are
– Can SiC be modified to be more machinable?? Stay Tuned!!!

Acknowledgements

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